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CONNECTION BETWEEN NITRATION REACTIONS AND OXIDATION OF SATURATED HYDROCARBONS BY NITRIC ACID

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[Relationships underlying the nitration of saturated hydrocarbons are of importance, because the resulting nitro derivatives may either serve as additives to diesel fuels (which improve the performance of the latter), or as monopropellants for rockets. Results clarifying the mechanism of the oxidation of low boiling hydrocarbons with nitric acid or with intermediate products formed in the course of a combined nitration and oxidation may also be conceivably utilized in work on rocket bipropellants]

We have shown before [1, 2] that in the interaction of isooctane (2, 2, 4-trimethylpentane) with dilute nitric acid, according to M. I. Konovalov, the following products are principally formed:

Nitro compounds including secondary nitroisooctane, tertiary nitroisooctane, secondary-tertiary dinitroisooctane, and a small quantity of nitromethane.

Ketones including acetone, 2, 2, 4-trimethylpentanone-3, and 2, 2-dimethylpentanone-4.

Acids including acetic, isobutyric, trimethylacetic, tert-butyl acetic, alpha, alpha-dimethyl succinic, and oxalic.

The results of the investigation in question permit a new approach to the question about the connection between the reactions of nitration and oxidation occurring when saturated hydrocarbons are acted upon by nitric acid, so that a substantial clarification of the subject becomes possible.

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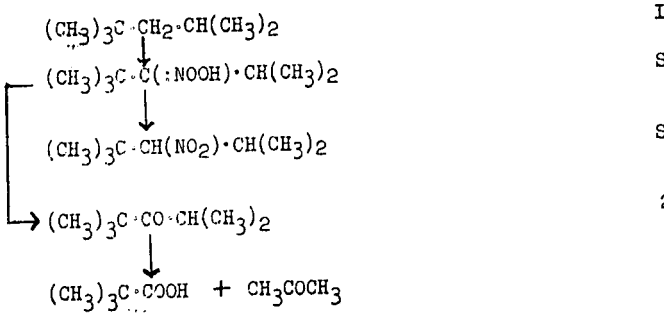
M. I. Konovalov, who discovered the nitrating effect of nitric acid on saturated hydrocarbons and has studied the nitration reaction on a great number of aliphatic and aliphatic-aromatic hydrocarbons, expressed the opinion that nitric acid first nitrates and then oxidizes, the nitro compounds thus representing the initial products of the reaction [3].

Much later S. S. Nametkin, who has studied the reaction chiefly on naphthenes, introduced a fundamental change into its interpretation. Pointing out that nitro derivatives of saturated hydrocarbons, for instance nitrocyclohexane, are extremely stable towards nitric acid even when boiled and are oxidized much more slowly than the corresponding hydrocarbons themselves (for example, cyclohexane), he expressed the opinion that the intermediate products formed in the oxidation of saturated hydrocarbons with nitric acid must be isonitro derivatives rather than nitro compounds. The isonitro derivatives, being unstable in the presence of acid, are then immediately isomerized into the corresponding nitro compounds, or else decomposed according to Neff's reaction with the formation of nitrogen monoxide (N_2O) and ketones or aldehydes. The ketones and aldehydes are subsequently oxidized into carboxylic acids. The isolation of ketones and aldehydes together with nitrogen monoxide from the reaction products is important evidence showing that isonitro derivatives are the initial products, provided that the effect of nitric acid is exerted at $=CH_2$ or $-CH_3$ groups, so that isonitro derivatives may actually form.

In the case of isooctane, this direction of the reaction, involving the intermediate formation of isonitro isooctane, leads to the formation of the only secondary nitroisooctane which may be expected here, namely 2, 2, 4-trimethyl-3-nitropentane. From the latter, the corresponding ketone 2, 2, 4-trimethyl-pentanone-3 and its oxidation products, trimethyl acetic acid and acetone, are formed. The last four products were actually found by us in the products of the interaction of isooctane with nitric acid.



In regard to the reaction scheme outlined above, isobutyric acid is apparently formed from the 2, 2, 4-trimethyl-pentanone-3.

The reaction proceeds differently when the tertiary hydrogen atom is attacked by the nitric acid. In this case, formation of an intermediate isonitro stage is impossible and the tertiary nitro compound is formed directly. The question arises as to whether tertiary nitro compounds may be a source of the formation of oxidation products derived from the initial hydrocarbon. Consideration of combined results on the composition of neutral and acidic products of the interaction of isooctane with nitric acid permits us to give an affirmative answer to this question.

As we have shown earlier [1], the tertiary nitroisooctane $C_8H_{17}NO_2$, upon heating with dilute nitric acid or water, is converted into 2, 2-dimethylpentanone-4 $C_7H_{14}O$ under splitting off of the constituents of nitromethane CH_3NO_2. Further oxidation of 2, 2-dimethylpentanone-4 must result in the formation of

tertiary butyl acetic acid and, subsequently, to that of alpha, alpha-dimethyl succinic acid. By investigating the acidic oxidation products resulting from tertiary nitroisooctane, it was found that these reactions actually take place according to the scheme outlined below:

Tertiary nitroisooctane

2, 2-dimethylpentanone-4

tert-butyl acetic acid + CO_2

alpha, alpha-dimethyl succinic acid

Thus, we succeeded in confirming, on the complex example of isooctane, that there is a connection between the reactions of nitration and oxidation with dilute nitric acid. The conversion proceeds not only according to the old scheme involving formation of an isonitro compound, but also in conformity with a new scheme over a tertiary nitro compound $C_8H_{17}NO_2$ (tertiary nitroisooctane) and the ketone $C_7H_{14}O$ (2, 2-dimethylpentanone-4), with subsequent transition to normal products of the oxidation of this ketone.

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